CHAPTER – V
RESULTS AND DISCUSSIONS

5.1. Magnetic properties of cobalt substitution on the Ni-Zn ferrites:

Cobalt substituted Ni-Zn (Nickel- zinc ) ferrite samples having the chemical formula $\text{Ni}_{0.95-x}\text{Zn}_{0.05}\text{Co}_x\text{Fe}_2\text{O}_4$ and $\text{Zn}_{0.95-x}\text{Ni}_{0.05}\text{Co}_x\text{Fe}_2\text{O}_4$, where $x$ varies as $x= 0.01, 0.02, 0.03, 0.04, 0.05$ and $0.06$ were prepared by the soft chemical route method. The formation of the ferrite phase was confirmed by x-ray diffraction (XRD) studies. The present samples belong to cubic system of ferromagnetic spinals. In these systems the magnetic order is mainly due to an upper exchange interaction mechanism occurring between the metal ions in the ‘A’ and ‘B’ sub lattices. The substitution of $\text{Co}^{2+}$ ions, which has a preferential ‘B’ site occupancy results in the reduction of the exchange interaction between ‘A’ and ‘B’ sites. Hence magnetic properties of the fine particles can be varied by varying the degree of cobalt substitution.

5.1.a Room temperature magnetic parameters measurements of ZNCF and NZCF fine particles:

Magnetic parameters, namely the specific magnetization ($M_s$) remnant magnetization ($M_r$) and coercive field ($H_c$) of the prepared fine particles ZNCF and NZCF were measured at room temperature in a maximum field of 10 KG (10000 gauss). Magnetic properties of ZNCF and NZCF are strongly dependent on the cobalt concentration. The room temperature magnetization curves of ZNCF and NZCF are given in Fig.5.1.1 to Fig.5.1.6 and Fig. 5.1.7 to Fig. 5.1.12 respectively. These show the variation of magnetization, coercive field with cobalt content.
Figures 5.1.1-5.1.6 : Magnetization curves of NZCF
The saturation magnetization ($M_s$) for ZNCF was found to decrease from $x=0.01$ to $x=0.03$, here is an increase in $M_s$ for $x=0.04$ and it is very low for $x=0.05$ and $x=0.06$ respectively. The $M_s$ for NZCF sample was found to
increase from $x=0.01$ to $x=0.02$ (upon cobalt substitution). For $x=0.03$, $M_s$ is very low. It is observed that the saturation magnetization decreases from $x=0.04$ to $x=0.06$. The respective reduction in magnetization can be due to a rearrangement of cations because of the changed preferential occupancy in the case of nanosized ferrites i.e., a change in distribution of $\text{Ni}^{2+}$ and $\text{Zn}^{2+}$ on the two sites.

The saturation magnetization of samples decreases with decrease in cobalt concentration ZNCF ($x=0.06$ to $x=0.03$) and NZCF ($x=0.06$ to $x=0.03$). This may be due to the relatively high orbital contribution of $\text{Co}^{2+}$ ions to the magnetic moment, which gives large induced anisotropy. In ferrites two magnetic ions are separated by nonmagnetic ion (in this case Oxygen). Hence magnetic ions have a magnetic interaction mediated by the electrons in their common nano magnetic neighbours, which is more important than their direct exchange interactions referred to as super exchange interaction. The presence of ions in the form of impurity (or) an absence of the oxygen ions at the surface leads to breakage of super exchange bonds between magnetic cations, including a large surface spin disorder (12). However, the low values of saturation magnetization obtained in the present work suggest that the mixed spinal structure is not likely to be present in our case. This plays an active role in the decline of magnetization values (13, 14). with the increasing cobalt incorporation the coercivity is showing a continuous increase, shown in Fig. 5.1.1 to Fig. 5.1.6 and Fig. 5.1.7 to Fig. 5.1.12 respectively for ZNCF and NZCF. This is attributed to the fact that coercive field ($H_c$) is directly
proportional to the magneto crystalline anisotropy constant. A small number of 
$\text{Co}^{2+}$ ions enter into the spinal lattice, leading to the appearance of the spin-
orbital coupling which determines the magnetic anisotropy in the ferrites. 
Therefore as the cobalt content increases, the magneto crystalline anisotropy 
increases, which decreases the domain wall energy resulting in high coercive 
force.

Reduction in the coercive field $M_r$ for ZNCF ($x=0.05$) and NZCF 
($x=0.06$) samples may be due to partial substitution of $\text{Co}^{2+}$ ion, due to size 
effect or due to the presence of super paramagnetic particles.

Another important factor which influences the magnetization of ferrites 
is the microstructure. The individual grain acts as magnetic dipole having 
certain amount of saturation magnetization. These grains form a magnetic 
circuit to produce resultant saturation magnetization. The presence of pores 
breaks the magnetic circuits present among the grains and results in a net 
reduction of magnetic properties with increasing pore concentration (15).

In this present report, the average grain size of the ferrite phase goes on 
increasing with cobalt content and results in a decrease in porosity; as a result 
saturation magnetization increases.

The magnetic order is mainly due to super exchange interaction 
mechanism occurring between metal ions in the A and B sub lattices. The 
change in magnetic property of $M_s$ is due to the influence of cationic 
stiochirometry and their occupancy in specific sites. The hysteresis curve 
recorded at room temperature shows very low remanance, coercivity for large
Cobalt concentration proves that the particles are super paramagnetic at room temperature.

5.1.b. Variation of initial Compositional permeability ($\mu_i$):

Initial permeability was determined by winding 100 turns of 30 SWG enamelled copper wire on toroids, and inductance measurement was carried out at various frequencies using a Hewlett Packard LCR-Q meter 4284A. $\mu_i$ was calculated using the relation (5). The $\mu_i$ measurements for compositional variation studies were carried out at room temperature, and in the case of thermal variation studies from room temperature to $450^0C$ at 1 kHz.

Figure 5.1.3 shows compositional variation of initial permeability measured at 1 kHz for the ferrite system $\text{Ni}_{0.95-x}\text{Zn}_{0.05}\text{Co}_x\text{Fe}_2\text{O}_4$, $\text{Zn}_{1-x}\text{Ni}_{0.05}\text{Co}_x\text{Fe}_2\text{O}_4$ (where $x = 0.00, 0.01, 0.02, 0.03, 0.04, 0.05$ and $0.06$). It is observed that the initial permeability decreases with increasing cobalt content. The decreasing trend in $\mu_i$ can be attributed to the domain wall energy, magneto crystalline anisotropy constant ($K_1$) and magnetostriction constant ($\lambda_s$).

Kulikowski et al [20] have observed with increasing cobalt content the domain wall energy increases and the value of initial permeability ($\mu_i$) decreases. There would also be expected a monotonic increase in $\lambda$ value. The contribution of cobalt ions to the magnetostriction of Ni–Zn ferrite has the same origin as the magneto crystalline anisotropy constant. The magnetostrictive effect is connected with cobalt ions which occupies octahedral sites of the spinal. Similar observations are observed in our case also.
Table 5.1. 1

<table>
<thead>
<tr>
<th>X</th>
<th>$\mu_i$</th>
<th>$\mu_{\text{eff}}$</th>
<th>$M_s$ RT (emu)</th>
<th>Grain size(D) $\mu$m</th>
<th>$K_1 \times 10^4$ S$\text{erg cm}^{-3}$</th>
<th>Density %</th>
<th>$\lambda_s$ $10^{-6}$</th>
<th>$n_B$</th>
<th>porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>80.3</td>
<td>51.23</td>
<td>402</td>
<td>1.52</td>
<td>-5.71</td>
<td>93.3</td>
<td>-16.21</td>
<td>4.41</td>
<td>7.9</td>
</tr>
<tr>
<td>0.02</td>
<td>61.5</td>
<td>46.11</td>
<td>395</td>
<td>1.71</td>
<td>-1.28</td>
<td>92.8</td>
<td>-16.88</td>
<td>4.21</td>
<td>7.3</td>
</tr>
<tr>
<td>0.03</td>
<td>60.1</td>
<td>42.20</td>
<td>422</td>
<td>1.58</td>
<td>3.28</td>
<td>93.6</td>
<td>-17.11</td>
<td>4.02</td>
<td>7.1</td>
</tr>
<tr>
<td>0.04</td>
<td>57.2</td>
<td>37.98</td>
<td>401</td>
<td>1.51</td>
<td>6.28</td>
<td>93.1</td>
<td>-17.68</td>
<td>4.16</td>
<td>7.7</td>
</tr>
<tr>
<td>0.05</td>
<td>49.8</td>
<td>37.21</td>
<td>412</td>
<td>1.31</td>
<td>8.88</td>
<td>91.2</td>
<td>-18.28</td>
<td>4.21</td>
<td>8.2</td>
</tr>
<tr>
<td>0.06</td>
<td>42.2</td>
<td>33.92</td>
<td>387</td>
<td>1.18</td>
<td>10.39</td>
<td>91.9</td>
<td>-19.99</td>
<td>4.09</td>
<td>8.1</td>
</tr>
</tbody>
</table>

Table 5.1. 2. Data on initial permeability ($\mu_i$), $\mu_{\text{eff}}$, $M_s$ (RT), grain size (D), magnetocrystalline anisotropy ($K_1$), density (%) and magnetostriction constant ($\lambda_s$) for the ZNCF system

<table>
<thead>
<tr>
<th>X</th>
<th>$\mu_i$</th>
<th>$\mu_{\text{eff}}$</th>
<th>$M_s$ RT (emu)</th>
<th>Grain size(D) $\mu$m</th>
<th>$K_1 \times 10^4$ S$\text{erg cm}^{-3}$</th>
<th>Density %</th>
<th>$\lambda_s$ $10^{-6}$</th>
<th>$n_B$</th>
<th>porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>129.5</td>
<td>72.2</td>
<td>331</td>
<td>1.62</td>
<td>-3.21</td>
<td>92.5</td>
<td>-8.92</td>
<td>3.28</td>
<td>7.21</td>
</tr>
<tr>
<td>0.02</td>
<td>119.6</td>
<td>71.19</td>
<td>328</td>
<td>1.81</td>
<td>0.72</td>
<td>93.1</td>
<td>-10.31</td>
<td>3.41</td>
<td>7.91</td>
</tr>
<tr>
<td>0.03</td>
<td>110.3</td>
<td>68.35</td>
<td>322</td>
<td>1.71</td>
<td>3.11</td>
<td>92.7</td>
<td>-11.21</td>
<td>3.22</td>
<td>6.75</td>
</tr>
<tr>
<td>0.04</td>
<td>95.8</td>
<td>62.23</td>
<td>313</td>
<td>1.68</td>
<td>5.89</td>
<td>93.4</td>
<td>-12.33</td>
<td>3.51</td>
<td>7.5</td>
</tr>
<tr>
<td>0.05</td>
<td>89.3</td>
<td>59.32</td>
<td>324</td>
<td>1.51</td>
<td>6.99</td>
<td>92.8</td>
<td>-13.17</td>
<td>3.61</td>
<td>7.3</td>
</tr>
<tr>
<td>0.06</td>
<td>81.1</td>
<td>50.21</td>
<td>319</td>
<td>1.33</td>
<td>11.73</td>
<td>93.2</td>
<td>-15.22</td>
<td>3.12</td>
<td>7.8</td>
</tr>
</tbody>
</table>

Table 5.1. 2. (b) Data on initial permeability ($\mu_{ii}$), $\mu_{\text{eff}}$, $M_s$ (RT), grain size (D), magnetocrystalline anisotropy ($K_1$), density (%) and magnetostriction constant ($\lambda_s$) for the ZNCF system
The values of \( K_1 \) are calculated by taking the end values of the corresponding ferrites and taking into consideration the stoichiometry of the composition. Initial permeability is expected to have a maximum between \( x = 0.01 \) and 0.02 for NZCF and for \( x = 0.00 \) and 0.01 for ZNCF. But this is not the case which is observed in our case which is clearly seen in figure 3a. Similar types of observation have been reported by Byan et al. [21]. They have suggested that the variation of initial permeability with cobalt content is not fully explained by the one-ion model and therefore another contribution to the magnetic anisotropy must exist.

It is interesting to note that van der Zaag [22] have observed a grain size of the same order for an Ni–Co–Zn ferrite and have established that grains are mono domains and initial permeability is predominantly rotational. It is therefore concluded that our system too is made of monodomains having
rotational permeability. In such a case, affecting the NMGB model [23–25] to eliminate the grain size effect, the values of $\mu_{\text{eff}} = \mu_i / (\mu_i \delta + D)$ are determined and are shown in tables 5.1.1-5.1.2. As $\text{Co}^{2+}$ content increases, the initial permeability $\mu_i$ decreases for a mixed Ni–Zn ferrite. This decrease in initial permeability $\mu_i$ may be due to the cobalt ion having positive magneto crystalline anisotropy $K_1$ and the addition of $\text{Co}^{2+}$ in a small quantity is expected to increase $\mu_i$ through compensation of the negative $K_1$ of excess Ni–Zn ferrite. However, the proportion of $\text{Co}^{2+}$ selected appears to cross the zero $K_1$ range and hence the $\mu_i$ shows a reverse trend. Therefore, a marginal contribution to $\mu_i$ may also come from $D$ (grain size) which tends to decrease.

Saturation magnetization $M_s$, however, does not show significant variation. On a bulk level the higher density will lead to high $\mu_i$ but there is no significant change in density to modulate $\mu_i$ significantly. Thus a decrease in $\mu_i$ is attributable to an increase in $K_1$. Thus $\mu_{\text{eff}}$ is modulated by $K_1$ and grain size. The decreasing $\mu_{\text{eff}}$ is due to an increase in $K_1$ and a decrease in grain size except for $x = 0.01$.

5.1.c. Thermal variation of initial permeability ($\mu_i$):

Figures 5.1.4–5.1.6 show the initial permeability $\mu_i$, its real part $\mu_i^1$, and imaginary part $\mu_i^{11}$ vary with temperature for the composition NZCF and ZNCF systems in the range from room temperature to the Curie temperature ($T_c$).
Near $T_c$, both $\mu_i$ and $\mu_{i1}$ drop to zero sharply. A sharp decrease in $\mu_i$ and $\mu_{i1}$ suggests single-phase formation of the ferrite material. This observation supports the conclusion drawn from the XRD analysis that all the compositions are single phase. In most of the magnetic materials, $\mu_i$ increase with temperature up to the Curie temperature $T_c$. This is because the anisotropy field usually decreases faster with temperature than $M_s$ [26]. Both Enz [27] and Ohta [28] have shown that the initial permeability $\mu_i$ is maximum at the temperature where the anisotropy constant changes sign.

From the thermal variation of $\mu_{i1}$, it is seen that with the increase of temperature $\mu_{i1}$ increases, reaches a maximum near $T_c$ and then falls sharply near to $T_c$. The loss becomes large near $T_c$, which may be due to the damping effect of the domain walls which may be very small. From thermal variation of the initial permeability for the composition NZCF and ZNCF systems with $x = 0.00, 0.01, 0.02, 0.03, 0.04, 0.05$ and $0.06$, peaking behaviour is observed at $T_c$. The Hopkinson peak indicates the presence of SD grains. Hence it can be concluded that there is dominance of SD grains. However, for detailed investigation the study of particle size distribution would have thrown light on an investigation. The variation in $\mu_i$ in our composition appears to be mainly due to variation of magneto crystalline anisotropy constant ($K_1$) and the grain size ($D$).
Figure 5.1.4. Thermal variation of initial permeability ($\mu_i$) for ferrite system

Figure 5.1.5. Thermal variation of initial permeability ($\mu_i^1$) for ZNCF system
5.1.d. Frequency dependence of initial permeability ($\mu_i$):

In figures 5.1.7 and 5.1.8 variation of $\mu_i^1$ and $\mu_i^{11}$ with frequency in the range 20 Hz–10 MHz, for the composition NZCF and ZNCF, are shown. Rado [29] and others [30–33] observed high frequency dispersion and absorption in $\mu_i$ and attributed it to rotational resonance in the combined anisotropy and demagnetizing fields while the low frequency dispersion was attributed to the domain wall displacement.

From figures 6a and 7a frequency variation of $\mu_i^1$ and $\mu_i^{11}$ clearly indicate the low frequency dispersion which may be attributed to the domain wall movement.

It is already shown that the major contribution to $\mu_i$ is due to domain wall displacement, which is manifested here by the low frequency dispersion. The dispersion at high frequencies (=1 MHz) is attributed to spin resonance in the internal anisotropy field.
5.1.e. Loss factor (LF):

The ratio of the imaginary part of the permeability representing the losses in the material to the real part of the permeability is a measure of the inefficiency of the magnetic system. It is called the loss tangent:

\[
\text{Loss tangent} = \tan \delta = \frac{\mu_i^1}{\mu_i^{11}}
\]

The loss factor is defined as

\[
LF = \frac{\tan \delta}{\mu_i}
\]

This loss factor (LF) parameter should be as low as possible.
In figure 5.1.9 dispersions of LF for the composition NZCF and ZNCF are shown. With the increase of frequency from 20 to 200 Hz, the LF decreases. In most of the compositions the LF value is almost constant in the frequency range 10–100 kHz. In figure 5.1.10 thermal variation of the loss
factor for the composition NZCF and ZNCF is shown. In the temperature range 25°C to near Tc, it is found that LF is almost constant, while above Tc the loss factor increases exponentially. The thermal variation of tan δ seems to be responsible for the increase in loss factor. In order to have a low loss factor the ferrite must be operated below the Curie temperature.
5.2 Dielectric Properties of Cobalt substituted Ni-Zn ferrites (NZCF) and (ZNCF):

The effect of frequency on the dielectric constant and dielectric loss factor is illustrated in figures 5.2a, 5.2b, 5.2c and 5.2d for NZCF and ZNCF systems respectively. The dielectric constant is found to decreases at lower frequencies and remains constant at higher frequencies, showing the usual dielectric dispersion. The dispersion of dielectric constant with frequency is due to Maxwell–Wagner [37, 38] type “interfacial polarization” in agreement with Koop’s phenomenological theory [39].

According to Rabinkin et al. [40], the polarization in ferrite is through a mechanism similar to the conduction process. The presence of Fe$^{3+}$ and Fe$^{2+}$ ions has rendered ferrite materials dipolar. Rotational displacement of dipoles results in orientation polarization. In ferrites, rotation of Fe$^{2+}$$\leftrightarrow$$Fe^{3+}$ dipoles may be visualized as the exchange of electrons between the ions so that the dipoles align themselves in response to the alternating field. The existence of inertia to the charge movement would cause relaxation of the polarization. The polarization at lower frequencies may result “from electron hopping” between Fe$^{2+}$$\leftrightarrow$$Fe^{3+}$ ions in the ferrite lattice. The polarization decreases with increase in frequency and reaches a constant value due to the fact that beyond a certain frequency of external field the electron exchange Fe$^{3+}$$\leftrightarrow$$Fe^{2+}$ cannot follow the alternating field [37]. In the present system, the presence of Ni$^{3+}$/Ni$^{2+}$ and Co$^{3+}$/Co$^{2+}$ ions gives rise to p-type carriers. The local displacement of p-type carriers in the direction of an external electric field also contributes to net
polarization in addition to that of the n-type carriers. However, the contribution due to p-type carriers should be smaller than the electronic exchange between Fe$^{3+}$/ Fe$^{2+}$ and has an opposite sign. Since the mobility of p-type carriers is smaller than n-type carriers, their contribution to the polarization decreases more rapidly even at lower frequencies. As a result the net polarization increases initially and then decreases with increase in frequency, as is observed in the present system. Similar results were reported earlier by Popandian et al [37].

Figure 5.2a Variation of dielectric constant of NZCF system with frequency
Iwauchi [41] and Rezlescu et al [35] have established a strong correlation between the conduction mechanism and dielectric behaviour of ferrites. The electronic exchange in these ferrites results in the local displacement of charges in the direction of the applied field, which determines the polarization of the ferrites. As both electrical conductivity and dielectric behaviour are transport properties and their variation with composition is similar, it may be presumed that the same mechanism is responsible for these phenomena. The resistivity and dielectric constant show an inverse trend of variation with cobalt content due to their inverse interdependence.

The variation of $\tan \delta$ with frequency shows a similar nature as the variation of $\varepsilon'$ with frequency. The loss factor is considered to be caused “by domain wall resonance”. At higher frequencies, losses are found to be low since domain wall motion is inhibited and magnetization is forced to change by rotation.

**Figure 5.2b** Variation of dielectric constant of ZNCF system with frequency
To understand the conduction mechanism and the type of polarons responsible for conduction, the variation of AC conductivity as a function of frequency is represented in figure 5.2(e) and 5.2(f) for NZCF and ZNCF systems respectively. It is well known that AC conductivity in disordered solids is directly proportional to frequency.
The electrical conduction mechanism in terms of the electron and polaron hopping model has been discussed earlier by Austin and Mott [42]. The plots of AC conductivity are linear, indicating that the conduction is due to small polarons. However, a slight decrease in conductivity at certain frequencies is attributed to mixed polaron (small and large) conduction [34]. The frequency-dependent conduction is attributed to small polarons, as reported by Alder and Fienleib [43]. At higher frequencies, where conductivity increases greatly with frequency, the transport is dominated by contributions from hopping infinite clusters.

**Figure 5.2(e)** Variation of AC conductivity of NZCF ferrite system
5.2.a Complex impedance:

Typical “room-temperature complex impedance spectra” for the samples with \( x = 0.01, 0.02 \) and 0.03 are shown in figures 5.2g. In the present investigation a well resolved semicircle is observed for each sample between the frequency range 20 Hz–1 MHz The “size of the semicircle changes with grain size”. The presence of a single semicircular arc obtained at higher frequencies corresponds to electrical conduction by the interior of the bulk grain. The diameter of the semicircle corresponds to the resistance of the grain [44]. As the cobalt content increases, the diameter of the semicircle decreases, indicating a reduction of the grain interior resistance. The observed semicircle can be modelled by an equivalent circuit consisting of a parallel combination of bulk resistance \((R_g)\) and bulk capacitance \((C_g)\), which is shown in the inset of figure 9(a) for 0.01 to 0.03 samples of NZCF. This RC equivalent circuit accurately fits each Cole–Cole semicircle. The fitting procedure used here is similar to the one described by Kleitz et al [45].
The real ($Z'$) and imaginary ($Z''$) parts of the complex impedances were calculated using the following equations [46]:

$$Z = Z' - jZ''$$

(a)

$$Z' = \frac{R_g}{1 + R_g^2 \omega^2 C_g^2}$$

(b)

$$Z'' = \frac{R_g^2 \omega C_g}{1 + R_g^2 \omega^2 C_g^2}$$

(c)

Where $\omega$ is the angular frequency. The impedance plot corresponding to calculated values of $Z'$ and $Z''$ are shown by open squares (figures 6.1(g)(a)–(c)). The observed and calculated complex impedance data match each other fairly well.
Figure 5.2(g) Variation of complex impedance for (a) $x = 0.01$, (b) $x = 0.02$ and (c) $x = 0.03$ at room temperature(NZCF)

5.2.b Dielectric Dispersion:

The variation of dielectric properties with frequency is depicted in figure 5.2(h)(1-6). It can be seen that the relative dielectric permittivity, $\varepsilon^1$ exhibits an inverse dependence with frequency as reported in a number of ferrite compounds. It decreases with increase in frequency and remains a constant at higher frequencies. In our frequency regime of measurements (100 kHz - 8 MHz), it is the polarization due to interface dipoles which contribute to the overall dielectric properties of the sample [50, 51]. Earlier, theories like Maxwell Wagner theory of dielectric dispersion were employed to study the dispersion [47, 48]. It was assumed that the dielectric polarization had its origin in the heterogeneous structure of ferrites with grains and grain boundaries [52]. The effect of grain interfaces are more pronounced at lower frequencies where we observe relatively large values of $\varepsilon^1$. The space charge polarization occurring at the interfaces at lower frequencies can also contribute to the dielectric permittivity at lower frequencies. Many researchers have reported a similarity between conduction process and dielectric polarization in ferrites.
Normally, for Manganese zinc ferrites, the conduction process is explained on the basis of electron hopping between $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ and hole hopping between $\text{Ni}^{2+}$ and $\text{Ni}^{3+}$ ions on the octahedral sites. In the Rezlescue Model, the hopping of electrons holes results in the local displacements of the electrons, holes which collectively contribute to the total polarization [53]. Denecke et al observed the presence of $\text{Mn}^{1+}$ions in octahedral sites in co-precipitated manganese zinc ferrite nanoparticles prepared using highly basic solution [54]. The electrons exchanging between $\text{Fe}^{2+}$and $\text{Fe}^{3+}$ ions and the holes that transfer between $\text{Ni}^{2+}$ and $\text{Ni}^{3+}$ions are responsible for electric conduction and dielectric polarization in manganese zinc ferrites. At higher frequencies, the frequency of electron / hole exchange will not be able to follow the applied electric field thus resulting in a decrease in polarization. Consequently the dielectric permittivity attains a constant value.

The temperature dependence of $\varepsilon^1$ at selected frequencies is shown in figure 5.2(i)(1-6). As the temperature increases, the orientations of interface dipoles are facilitated and this enhances the dielectric permittivity. At lower frequencies the rapid increase in dielectric constant with temperature is mainly due to polarization due to interfacial dipoles which are strongly dependent on temperature [51]. As temperature increases, the accumulation of charges on the grain boundaries increases which causes an increase in the interfacial polarization. This is at lower frequencies. Therefore the dielectric polarization increases resulting in an increase of $\varepsilon^1$ with temperature at lower frequencies.
Figure 5.2(h) (1-6) Variation of Dielectric properties with frequencies of the Ni-Zn ferrite system
Figure 5.2(i)(1-6). Dielectric permittivity vs. Temperature plot of Ni-Zn ferrite system (NZCF)
5.2.c Dielectric Absorption:

Dielectric absorption in a material is characterized by tan δ and dielectric loss (ε₁₁) values. It can be seen that tan δ and ε₁₁ values when plotted against frequency exhibit relaxations at specific frequencies and temperatures (figure 5.2(j)(1-6) and 5.2(k)(1-6). Dielectric relaxation occurs when the hopping frequency of charge carriers is equal to the frequency of the applied field [55]. However it is to be noted that a relaxation can be noticed in the case of manganese rich compositions while for the zinc rich compositions the relaxation is found to be absent. This may be due to the reduction in number of hopping charges available for hopping as the zinc concentration increases. There also is a likelihood that the relaxation peaks corresponding to these compositions lie outside the frequency range of measurement.
Figure 5.2(j)(1-6) Tan δ vs. Temperature plots of Ni-Zn ferrite systems
Figure 5.2(k)(1-6) Dielectric loss Vs. log (f) plots of Ni-Zn ferrite system
5.2.d Effect of Cobalt Substitution On dielectric properties:

The Cobalt substitution has a direct influence in modifying the dielectric characteristics. The variation of $E$ with Cobalt compositions is studied for different temperatures and different frequencies [figure 5.2(L) (a-b)] The dielectric permittivity decreases with increase in Cobalt content. With increasing Cobalt content there is a decrease in Cobalt ions and consequently the presence of Fe$^{2+}$ ions in the octahedral sites is also reduced. Hence the number of Co$^{3+}$,Co$^{2+}$ and Fe$^{3+}$,Fe$^{2+}$ pairs available for “hole and electron hopping” will be less in number as we increase the Cobalt content. As a result hopping decreases and the charged species are accumulated at the grain boundaries. Therefore the resistance of the grain boundaries increases and hence the probability of charged species to cross over the grain boundaries decreases. These will subsequently result in “reduced hopping” and “dielectric polarization” which is manifested in “low permittivity” values in zinc rich compositions.
Figure 5.2(L)(a) Dielectric permittivity Vs cobalt content for NZCF system

Figure 5.2(L)(b) Dielectric permittivity Vs cobalt content for ZNCF system
Figure 5.2(m) (a) tan δ Vs cobalt content for NZCF system

Figure 5.2(m) (b) tan δ Vs cobalt content for ZNCF system
Figure 5.2(n)(a) tan δ Vs cobalt content for NZCF system

Figure 5.2(n)(b) tan δ Vs cobalt content for ZNCF system

Figure 5.2(m) (a-b) and 5.2(n) (a-b) depicts the effect of Cobalt substitution on the tanδ and dielectric permittivity of the NZCF and ZNCF ferrite series. A reduction in dielectric absorption values is seen with an increase in Cobalt concentration. A decrease in the Fe³⁺/Fe²⁺ and Ni³⁺/Ni²⁺ pairs available for conduction with increase in Cobalt concentration can be
thought of as one of the reasons for this type of behaviour in Nickel zinc ferrites.

We have suggested that the dielectric polarization can be explained based on the hopping of charge carriers. A relaxation occurs when the hopping frequency equals the applied frequency. The evaluation of the activation energy can provide more insight on the transport properties of ferrites [56].
5.3 Electrical properties of Cobalt substituted Ni-Zn ferrites (NZCF) and (ZNCF):

Ferrites have vast applications from microwave to radio frequencies (57). They possess high resistivity up to $10^9 \Omega\text{cm}$ at room temperature which contributes to very low losses needed for microwave. Verwey (58) suggested the hopping motion of electrons between Fe$^{2+}$ and Fe$^{3+}$ over octahedral site as a mechanism of conduction in ferrite. Ferrites are semiconductors, their electrical resistivity ($\rho_0$) decreases with increase in temperature according to the relation $\rho=\rho_0 \exp (\Delta E/KT)$ (59,60), where $\Delta E$ is the activation energy, $\rho_0$ is the temperature dependent constant and K is Boltzmann constant. We have studied the chemical compositions NZCF and ZNCF, where $x$ varies from $x=0.01$ to $0.06$. The resistivity is found high and magnetic losses caused by eddy currents are negligible. The electrical conductivity depends upon the method of preparation, amount of impurities, stoichiometry and temperature (61-64). Hence it is interesting to study these properties. In this present study, we report the studies on dc electrical resistivity ($\rho_{dc}$), frequency and ac electrical resistivity ($\rho_{ac}$).

It is observed that the lattice parameters increase with the addition of Co$^{2+}$ content for Ni-Zn ferrites, which can be attributed to larger ionic radius of Co$^{2+}$ (0.78 Å) than Ni$^{2+}$ (0.74 Å). The linear variation of lattice parameter with respect to concentration fulfils the condition of Vegard’s law. The observed values of room temperature dc resistivity are summarized in Table 5.3.1 and
Table 5.3.2. It is seen that the dc resistivity ($\rho_{dc}$) increase as Co$^{2+}$ concentration increases in ZNCF and in NZCF ferrites up to $x=0.04$.

**Table 5.3.1** Structural and Electrical properties of NZCF ferrites

<table>
<thead>
<tr>
<th>$x$</th>
<th>Lattice parameter</th>
<th>$\rho_{dc} \times 10^{7}$ Ω cm At Room temp</th>
<th>Ferro $E_i(\Delta E)$ in (ev)</th>
<th>Para $E_2(\Delta E)$ in (ev)</th>
<th>$\Delta E = \Delta E_2 - \Delta E_1$ (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>8.387</td>
<td>1.3</td>
<td>0.03</td>
<td>0.81</td>
<td>0.78</td>
</tr>
<tr>
<td>0.02</td>
<td>8.389</td>
<td>5.6</td>
<td>0.04</td>
<td>0.85</td>
<td>0.81</td>
</tr>
<tr>
<td>0.03</td>
<td>8.392</td>
<td>25.6</td>
<td>0.08</td>
<td>0.51</td>
<td>0.43</td>
</tr>
<tr>
<td>0.04</td>
<td>8.395</td>
<td>55.3</td>
<td>0.21</td>
<td>0.59</td>
<td>0.38</td>
</tr>
<tr>
<td>0.05</td>
<td>8.396</td>
<td>3.6</td>
<td>0.17</td>
<td>0.42</td>
<td>0.25</td>
</tr>
<tr>
<td>0.06</td>
<td>8.398</td>
<td>2.0</td>
<td>0.17</td>
<td>0.68</td>
<td>0.51</td>
</tr>
</tbody>
</table>

**Table 5.3.2** Structural and Electrical properties of ZNCF ferrites

<table>
<thead>
<tr>
<th>$x$</th>
<th>Lattice parameter</th>
<th>$\rho_{dc} \times 10^{7}$ Ω cm At Room temp</th>
<th>Ferro $E_i(\Delta E)$ in (ev)</th>
<th>Para $E_2(\Delta E)$ in (ev)</th>
<th>$\Delta E = \Delta E_2 - \Delta E_1$ (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>8.388</td>
<td>3.2</td>
<td>0.37</td>
<td>0.40</td>
<td>0.03</td>
</tr>
<tr>
<td>0.02</td>
<td>8.390</td>
<td>6.5</td>
<td>0.37</td>
<td>0.43</td>
<td>0.06</td>
</tr>
<tr>
<td>0.03</td>
<td>8.393</td>
<td>7.0</td>
<td>0.37</td>
<td>0.48</td>
<td>0.11</td>
</tr>
<tr>
<td>0.04</td>
<td>8.394</td>
<td>7.4</td>
<td>0.39</td>
<td>0.51</td>
<td>0.12</td>
</tr>
<tr>
<td>0.05</td>
<td>8.398</td>
<td>18.4</td>
<td>0.40</td>
<td>0.52</td>
<td>0.12</td>
</tr>
<tr>
<td>0.06</td>
<td>8.399</td>
<td>35.7</td>
<td>0.36</td>
<td>0.59</td>
<td>0.23</td>
</tr>
</tbody>
</table>

The conduction in these ferrites can be explained by the Verwey mechanism (65). A very small amount of Fe$^{2+}$ and Ni$^{3+}$ are formed during the sintering process and electron exchange is believed to be between the iron ions and nickel ions (58), which can be written as $\text{Ni}^{2+} + \text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+} + \text{Ni}^{3+}$. The increase in resistivity with increase in cobalt content is due to the formation of stable electric bonds between the Co$^{2+}$ and Fe$^{2+}$ ions, which localizes Fe$^{2+}$ charge carriers. This in turn hinders the verwey mechanism, thereby increasing resistivity. In case of ZNCF the resistivity increases. This increase in resistivity
of the sample is due to the formation of Fe$^{2+}$ ions which gives rise to electron hopping between Fe$^{2+}$ and Fe$^{3+}$ ions.

Fig. (5.3.1) shows the variation of dc resistivity with temperature for ZNCF. It is seen that the variation in dc resistivity is almost linear up to ~600K where a break occurs. This break corresponds to a magnetic ordering from ferromagnetism to paramagnetism. The calculated values for both ferro and para activation energy ($\Delta E$) are tabulated in Tables (5.3.1) and (5.3.2) For NZCF and ZNCF ferrites respectively, the values of $\Delta E$ is paramagnetic region is found to be greater than those observed in ferromagnetic region. This suggests that the process of conduction is affected by change in the magnetic ordering. The $\Delta E$ and resistivity are found to increase with increase in cobalt content. The magnitude of activation energy for both the compositions with Co$^{2+}$ content lies between 0.36 to 0.59 eV which suggests that the conduction process in the present ferrites is due to hopping of polaron.
Fig 5.3.1 Variation of dc resistivity with temperature for the Ni-zn system

It was reported that the magnetic Ni$^{2+}$ ion strongly prefers the occupation of B-sites (66-68) and the magnetic Fe$^{3+}$ ion partially occupies tetrahedral sites A-sites and B-sites (69-73), while the non-magnetic Zn$^{2+}$ ion strongly prefers the occupancy of A-sites (69-73). The electron hopping between Fe$^{2+}$ and Fe$^{3+}$ ions (n-type) and hole hopping between Ni$^{3+}$ and Ni$^{2+}$ (p-type) on B-site are responsible for electric conduction and dielectric polarization (74). As Co$^{2+}$ ion substitution increases replacing Ni$^{2+}$ ions, some of Fe$^{3+}$ ions are likely to be forced to migrate from B-site to A-sites (75). As a result, the number of Fe$^{2+}$ and Fe$^{3+}$ ions increases while the number of Ni$^{3+}$ and Ni$^{2+}$ ions decrease as Co$^{2+}$ ion substitution increases. Therefore, the local displacement (dielectric polarization) in the direction of applied electric field
(for electrons) decreases. This explains the decrease in $\varepsilon_1$ and $\tan \delta$ as $\text{Co}^{2+}$ ion substitution increases as explained in NZCF/ZNCF ferrite system of dielectric properties of these ferrites.

Fig.(5.3.2) shows the variation of ac resistivity $\rho_{dc}$ as a function of applied frequency measured at room temperature for ZNCF series. In all the composition of this series the “ac resistivity decreases with increasing frequency” and then it remains invariant at high frequencies ($> 100$ kHz). From Fig.(5.3.2) it is clear that in the low frequency region ac resistivity increases with increase in composition parameter $x$. The composition between lower frequency region of variation of real dielectric constant $\varepsilon_1$ with frequency fig (5.2h) of dielectric properties and variation of resistivity with frequency Fig(5.3.2) show opposite trends for dielectric constant and ac resistivity with respect to the composition.

![Graph showing variation of ac resistivity with frequency for ni-zn system](image)

**Fig. 5.3.2** Variation of ac resistivity ($\rho_{ac}$) with frequency for ni-zn system
The curie temperature data for the composition of NZCF and ZNCF determined from the dc resistivity and initial permeability measurements are represented in tables 5.3.4 and 5.3.5. It was observed that the curie temperature decreases with increase in Co^{2+} concentration for both the series. This can be explained on the basis of curie temperature of NiFe_2O_4 and CoFe_2O_4 as the curie temperature of CoFe_2O_4 (525°C) is less than that of NiFe_2O_4 (525°C). The decreasing trend is expected with increasing Co^{2+} concentrations.

The exchange energy $K_T$ also decreases with the increase in Co^{2+} content implies the weakening of A-B exchange interaction from Fe^{3+}_A–O^2-fe^{3+}_B linkages. In other words, the thermal energy required to offset the spin alignment decreases, the curie temperature also decreases. It is also observed that systematic decrease in $T_c$ with increasing Zinc is due to the dilution of A lattice magnetic moment and subsequent Weakening of AB super
lattice exchange interaction. Similar observations have been reported by Murthy et al (75).

**Table 5.3.4**: Data on Curie temperature by dc resistivity and permeability measurement and $K_T_c$ values for NZCF system

<table>
<thead>
<tr>
<th>x</th>
<th>Curie temperature</th>
<th>Curie temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_c$ (°C)</td>
<td>$T_c$ (°C)</td>
</tr>
<tr>
<td></td>
<td>Dc resistivity</td>
<td>permeability</td>
</tr>
<tr>
<td>0.01</td>
<td>5.05</td>
<td>61</td>
</tr>
<tr>
<td>0.02</td>
<td>5.605</td>
<td>57</td>
</tr>
<tr>
<td>0.03</td>
<td>5.627</td>
<td>50</td>
</tr>
<tr>
<td>0.04</td>
<td>5.75</td>
<td>43</td>
</tr>
<tr>
<td>0.05</td>
<td>5.832</td>
<td>30</td>
</tr>
<tr>
<td>0.06</td>
<td>6.112</td>
<td>25</td>
</tr>
</tbody>
</table>

**Table 5.3.5**: Data on Curie temperature by dc resistivity and permeability measurement and $K_T_c$ values for NZCF system

<table>
<thead>
<tr>
<th>x</th>
<th>Curie temperature</th>
<th>Curie temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_c$ (°C)</td>
<td>$T_c$ (°C)</td>
</tr>
<tr>
<td></td>
<td>Dc resistivity</td>
<td>permeability</td>
</tr>
<tr>
<td>0.01</td>
<td>5.21</td>
<td>63</td>
</tr>
<tr>
<td>0.02</td>
<td>5.582</td>
<td>59</td>
</tr>
<tr>
<td>0.03</td>
<td>5.615</td>
<td>52</td>
</tr>
<tr>
<td>0.04</td>
<td>5.725</td>
<td>46</td>
</tr>
<tr>
<td>0.05</td>
<td>5.79</td>
<td>35</td>
</tr>
<tr>
<td>0.06</td>
<td>6.121</td>
<td>28</td>
</tr>
</tbody>
</table>

**5.4 DC resistivity:**

The variation of DC resistivity with temperature for all the compositions is represented in fig (5.3.4). The plots show two slopes with a single transition at a temperature, which is close to the cure temperature of the ferrites (76)

Fig (5.3.1) shows the variation of Dc resistivity with temperature in NZCF ferrites. The conduction mechanism in ferrites is explained on the basis of the Verwey de Boer (83) mechanism that involves exchange of electrons
between the four of the same elements present in more than one valancy state and distributed anomaly over equivalent crystallographic lattice sites. The decrease in resistivity with temperature is due to the increase in drift mobility of the charge carriers. Also, conduction in ferrites is attributed to hopping of electrons from \( \text{Fe}^{3+} \) and \( \text{Fe}^{2+} \) ions (84). The resistivity of ferrites is controlled by the \( \text{Fe}^{2+} \) concentration on the B-site.

The variation of room temperature DC resistivity with cobalt content is shown in Fig.(5.3.4) The decrease in DC resistivity may be attributed to the changes in cation distribution, formation of excess \( \text{Fe}^{2+} \) ions and the difference in ionic size of the cations. Due to the higher ionic size of Co as compared to Ni, Zn and Fe, its addition distorts the ferrite lattice. The distribution can affect the motion of charges causing a change in resistivity (82).

![Graph showing variation of resistivity and activation energy with cobalt content.](image)

**Figure 5.3.4** Variation of room-temperature DC resistivity and activation energy with cobalt content.
In ferrites, the electrons are localized and there is little overlap between the wave functions of ions situated on adjacent sites. In the presence of lattice vibration, the ions occasionally come so close that the transfer of electrons from one ion to another occurs with high probability. Hence the mobility is temperature dependent and is characterized by activation energy. The lowering of activation energy in the ferromagnetic region is attributed to the affect of spin disordering (81). It is well known that the electron and hole hopping between the Fe$^{2+}$/Fe$^{3+}$, Ni$^{3+}$/Ni$^{2+}$, Zn$^{3+}$/Zn$^{2+}$ and Co$^{3+}$/Co$^{2+}$ with an activation energy $\approx 0.2$ eV, is responsible for electron conduction in mixed ferrites (85). The present values of activation energies suggest that the hopping of small polarons is responsible for the conduction in NZCF and ZNCF ferrites.

The activation energies for conduction was computed from log $\rho$ Vs 1000/T plots and are presented in graph(5.3.1). The activation energy increases on changing from the ferromagnetic to para magnetic region. The high value of the activation energy in the paramagnetic state as compared to the ferromagnetic state is due to the volume expansion of the samples during the magnetic transition (77-79). The activation energies in the ferromagnetic region are much higher than the ionization energies ($E_i = 0.1$ eV) of donors (acceptors as and also higher than the transition of Fe$^{2+}$ and Fe$^{3+}$ ($E_c = 0.2$eV) that the polaron type conduction mechanism is formed.

The AC conductivity of the samples was calculated from the dielectric parameters using the relation

$$\sigma_c = \epsilon' \epsilon_0 \omega \tan \delta$$

5.3.1
Where $\varepsilon_1$ is dielectric constant, $\varepsilon_0$ permittivity of free space, $\omega$ the angular frequency, $\tan \delta$ is the loss tangent. Fig (5.3.5) shows the frequency dependent variation of AC conductivity.

![Graph](image)

**Fig. 5.3.5** Variation of AC conductivity of Ni-Zn system with frequency

The conductivity for all the compositions under study, linear variation of AC conductivity indicates that the conduction occurs by hopping of charge carriers among localized states. Adler and Feinleib (80) have shown that for conduction by small polarons. AC conductivity increases with frequency linearly. Hence it is concluded that the conduction is due to small polarons.
References:
1. Caizer C and Stefensen M 2002 j.Phy.D ; Appl.phy 35 3035
   (Tokyo and yoto, Japan)
6. Shinde R S, Bhasin H K and Karmarkar M G 1997 7th Int. Conf. on
   Ferrites (Bordeaux, France); J. Phys. IV France 7 C1-149–50
7. Shinde R S, Pareek P and Yadav R R 2004 Proc. APAC (Gyeongju, Korea) p 699
    Hagenmuller (New York: Academic) p 487
    Overview (Advances in Chemistry Series) (Washington, DC: American
    Chemical Society) p 139
    (New York: McGraw-Hill) p 152
    Polycrystalline and Amorphous Materials (New York: Wiley) p 491
29. Rado G T 1953 Rev. Mod. Phys. 25 81
32. Rado G T, Wright R W and Emerson W H 1950 Phys. Rev. 80 273
38. Koops C G 1951 Phys. Rev. 83 121
   (Amsterdam: North-Holland)
46. KW Wagner, Ann. Physics, 40, (1913),817
47. C G Koops Physical Review, 83, (1951),121
48. B Vishwanathan, V R K Moorthy, Ferrite Materials :Science and
   Technology, Springer Verlag 1990
49. Hari Singh Nalwa, Encyclopedia of Nanoscience and Nanotechnology,
50. H Fang, B Chen, K Jiang, J Sha, Z Jiao, Q Zhang and L Zhang, Phys
51. Z P A Miles, W B West Phal and A Von Hippel, Reviews of modern
    Physics, 29, (1957), 279.
53. Mellisa. A Denecke, W Gun Ber, G Buxbaum, P Kuske, Materials
57. R.G. Kharabe, R.S. Devan, C.M. Kanamadi, B.K. Chougule,
60. M.M. Mallapur, P.A. Shaikh, R.C. Kambale, H.V. Jamadar, P.U.